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*This article is presented in English with abstracts in Spanish and Portuguese**Brazilian Journal of Applied Technology for Agricultural Science, Guarapuava-PR, v.7, n.1, p.103-111, 2014***Bibliographic Review****Abstract**

The anionic phosphate molecule presents a specific behavior in the soil, which is determinant in its movement in the soil and in provision to plants. Factors like soil texture and mineralogy directly affect the reactions of phosphate applied by fertilizers and the availability of the element in soil solution, where the molecular characteristics of the reagents imply on the differentiation of the final products of the reactions. Thus, phosphorus' molecular form present in different phosphate fertilizers differs, and may interfere in the plants absorption efficiency of this element depending on the conditions and chemical reactions on the soil. The comprehension of the product of these reactions in the soil can increase the phosphate efficiency, with reduced environmental impact and increase in crop productivity.

Keywords: phosphorus; phosphorus fertilizers; solubility.**Influence of different phosphorus sources on fertilization efficiency***Fernando Dubou Hansel¹**Telmo Jorge Carneiro Amado²**Rafael Pivotto Bortolotto³**Brian Santos Trindade⁴**Dâmaris Sulzbach Santos Hansel⁵***Influência de diferentes fontes fosfatadas na eficiência da fertilização****Resumo**

A molécula aniônica do fosfato apresenta um comportamento específico no solo, o qual é determinante em seu movimento no solo e o suprimento às plantas. Fatores como textura e mineralogia do solo governam diretamente as reações do fosfato adicionado através dos fertilizantes e a consequente disponibilidade do elemento na solução do solo, onde a característica molecular dos reagentes implica na diferenciação dos produtos finais das reações. Sendo assim, a forma molecular do fósforo contido em diferentes fertilizantes fosfatados diferem e podem interferir na eficiência da absorção deste elemento pelas plantas dependendo das condições e reações químicas decorrentes no solo. O entendimento do produto dessas reações no solo pode aumentar a eficiência da fertilização fosfatada, com reduzido impacto ambiental e incremento na produtividade das culturas.

Palavras-chave: fósforo; fertilizantes fosfatados; solubilidade.**Influencia de diferentes fuentes de fósforo en la eficiencia de la fertilización****Resumen**

La molécula de fosfato aniónico tiene un comportamiento específico en el suelo, que es crucial en su movimiento en el suelo y suministro a las plantas. Factores tales como la textura del suelo y la mineralogía gobiernan directamente las reacciones de los fertilizantes de fosfato añadido a través de la consiguiente disponibilidad del elemento en la solución del suelo, donde la característica molecular de reactivos implica en la diferenciación de los productos finales de las reacciones. Por lo tanto, las formas moleculares del fósforo contenidos en diferentes fertilizantes de fosfatados difieren y pueden interferir en la eficacia de absorción del elemento por las plantas dependiendo de las condiciones y reacciones químicas que resultan

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- 1 Agronomy Engineer, Doctorate student of the program of Post Graduation in Agronomical Engineering, Program of Post Graduation in Agronomical Engineering, Universidade Federal de Santa Maria, UFSM, Santa Maria, Rio Grande do Sul, Brasil. Roraima Boulevard. CEP: 97105-900. E-mail: fernandodhansel@gmail.com
- 2 Agronomy Engineer, Doctorate, Professor of Department of Soils, Universidade Federal de Santa Maria, UFSM. E-mail: florestatel@hotmail.com
- 3 Agronomy Engineer, Doctorate, Professor of Department of Soils, Universidade Federal de Santa Maria, UFSM. E-mail: rafaelpbortolotto@gmail.com
- 4 Agronomy Engineer, Doctorate student of the program of Post Graduation in Agronomical Engineering, Universidade Federal de Santa Maria, UFSM. E-mail: brianstrindade@hotmail.com
- 5 Agronomy Engineer, Masters student of the program of Post Graduation in Agronomical Engineering Universidade Federal de Santa Maria, UFSM. E-mail: damarissulzbach@hotmail.com

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en el suelo. Comprender el producto de estas reacciones en el suelo puede aumentar la eficiencia de la fertilización con P, reducir el impacto ambiental y aumentar la productividad de los cultivos.

Palabras clave: fósforo; fertilizantes fosfatados; solubilidad.

Introduction

Brazilian soils, due to its characteristics, present great dependence of phosphate fertilization for grains productivity, in such way that its use became essential for the plants to respond in high productivities. The soybean absorbs around 8.4 kg of phosphorus (P) for each Megagram of grains produced, being the most demanding crop in relation to wheat and maize crops (MALAVOLTA, 1980). Consequently, during the last decades, the increasing demand for phosphate fertilizers, allied to the great expansion of the world agriculture, resulted in diversification of the produced phosphates sources. The different acid processes provided in the phosphate concentrate of rock, result in varied compositions and concentrations of the fertilizer source, being considered after this treatment, sources of high solubility.

Somewhat, all soluble phosphate sources are rapidly solubilized on the soil, making available the P for plants absorption. However, the soluble P, in water, in the form of orthophosphate can be quickly converted in non soluble forms through reactions with minerals (RHEINHEIMER et al., 2003; BASTOS, 2006). Due to the variability of products of the reactions of P in the soil HEDLEY and MCLAUGHLIN, 2005), different soluble phosphate sources can present different efficiencies under adverse conditions, also dependent on the textural and mineralogical characteristics of the soil (CHIEN et al., 2011).

In a general manner, in studies with P are used the superphosphates as experimental standard (NUNES, 2010), not being considered the existing variability in the structural characteristics of the phosphate fertilizer molecule and the possible interactions with the manner of application (TRENKEL, 1997; DEITH et al., 2005). The variability existence in the composition of phosphate sources can result in equivocated conclusions in studies with fertilizers (CHIEN et al., 2011).

This revision approaches matters still little explored in the literature about the influence of the phosphate source in the product of the P reactions in the soil, in which the better understanding and

comprehension can lead to a more efficient and sustainable fertilizer management.

Form and movement of phosphorus in the soil

The P is found in the soil in two main forms: organic (Po) and inorganic (Pi). The Po is found in humus, in the soil biomass and in other organic materials, while the Pi occurs in several combinations with iron ions (Fe), aluminum (Al), calcium (Ca) and other elements, in the vast majority, whose confer to the P great structural stability and thus insolubility in water (DEITH et al., 2005). Both forms (Po and Pi) are important sources for plants growth, but its availabilities are controlled by the soil characteristics and by the environment conditions, which interfere mainly in the mineralization rate of the organic fraction by the microorganisms (STEWART and TIESSEN, 1987).

The main characteristic of the P dynamic in the soil is its immobility. Virtually all P in its soluble form, originated from fertilization or from organic residues is converted in the soil into insoluble forms, few hours after the application. According to MEURER et al. (2006), the phosphate anion reacts with reactive groups of OH⁻ surface (non-crystalline aluminosilicates, oxides and hydroxides of Fe, Al and Manganese (Mn) and the edges of silicate clay minerals), specifically absorbing the anion in the form of inner-sphere complexes. This reaction turns the P present in soil solution unavailable.

The roots absorb P ions in the anionic forms of H₂PO₄⁻ or HPO₄²⁻, commonly found in the pH ranges from 4.0 to 8.5 of the Brazilian soils (BARBER, 1984). The mineral supplementation of P to plants is determined by the soil capacity in replace the P in the soil solution (buffering capacity) and by management of phosphate fertilization, as well as by environmental and soil conditions, whose affect the bioavailability of P and the roots growth (DEITH et al., 2005). The plants ability of absorbing the P of the soil depends on the ions concentration in solution in the roots surface and on the area roots area in contact with the solution (JONES and JACOBSEN, 2001).

In the soil there are three main mechanisms of contact of the nutrients with the plants roots: root

interception, mass flow and diffusion (OLIVEIRA et al., 2004). The root interception occurs when the nutrients are intercepted by the roots during the growth process, however, the mechanism of root interception has not been considered, because actually it is not accepted the possibility of direct trades between the particles of soil and the roots of plants, existing need of half liquid so that the absorption by roots occur (RUIZ et al., 1999).

Mass flow refers to the leakage of a solute with soil water, that is, the water and the solute dissolved in it move at the same speed (RUIZ et al., 2010). The mass flow has being responsible for approximately 80% of N absorbed by plants and only 5% of P (FOTH and ELIIS, 1997). This suggests that the P (and other nutrients with lesser mobility) is somehow moving much faster than the surrounding water is, towards the roots (JONES and JACOBSEN, 2001). Therefore, the diffusion becomes responsible by the remainder of the nutrients movement.

The transportation of solutes through diffusion (molecular diffusion) is a spontaneous process, which results from the thermal and random movement of ions and molecules in the liquid stage of the soil, resultant from the difference of concentration between points in the soil solution (Figure 1), that is, the movement occurs in higher points of concentration for those of lower concentrations, such as happens close to the plants roots surface (RUIZ et al., 2010).

The nutrients which present higher dependence of the diffusive process in the transportation for plants roots are those of low mobility, which are in low concentration in the solution and are still necessary in great quantity for the plant, such as the P (JONES and JACOBSEN, 2001). In this sense, the great majority of P absorbed by the plant in originated from the diffusive transportation in soil, being this of huge importance for the plant nutrition and guarantee of response in grains yield.

The diffusivity of an ion in the soil can be estimated through the diffusion coefficient, where different factors can interfere in the value of the same, depending on the conditions of the diffusive means. LEWIS and QUIRK (1967), in a study approaching the factors that alter the coefficient of diffusion of phosphate in the soil, show that the same was markedly influenced by the level of phosphate addition, it is, by the phosphate concentration in the solution. Also, the magnitude of interaction between phosphate in the solution and the solid stage of

soil (clay minerals) was appointed as determinant factor, where the absorbed portion in the soil colloids proportionate a reduction of concentration of phosphate available in the solution, and consequently reduction of the diffusive flow (RUIZ et al., 1988; OLIVEIRA et al., 2004; COSTA et al., 2006).

The soil pH is another factor that modifies the diffusivity coefficient of phosphate in the soil, in a way that the same induces changes in the ionic species, from H_2PO_4^- to HPO_4^{2-} , which will probably result in mobility decrease of the phosphate (LEWIS and QUIRK, 1967), as well as the soil temperature, which interferes in the solubility and phosphate diffusion (GRANT et al., 2001).

According to COSTA et al. (2009), in a study of diffusivity of P in the soil in function of different fertilizer sources and volumetric content of water, in distinct soils, the diffusive flow varied with the source of element used, with the humidity and soil texture. Foremost, their results showed that the monoammonium phosphate source ($\text{NH}_4\text{H}_2\text{PO}_4$) presented higher coefficients of diffusivity, compared to the potassium phosphate (KH_2PO_4), being the lesser flow obtained with the monocalcium phosphate Ca (H_2PO_4)₂. Their conclusion was that the cation alongside with the anion interfered in the diffusive process of P in the soil, corroborating with LEWIS and QUIRK (1967). Subsequently, altering the volumetric humidity in the soil was verified great influence generated in the diffusion. The diffusion of an ion in the soil is directly related with the volumetric content of water, since this humidity determined the area fraction or the soil volume where occurs the diffusive flow (COSTA et al., 2006).

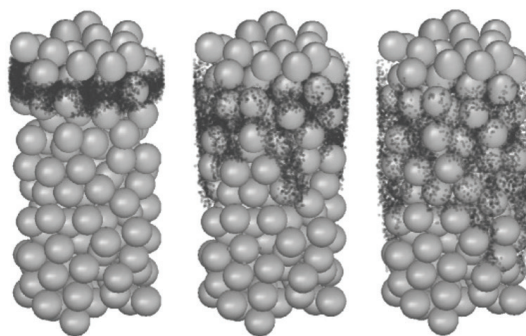


Figure 1. Demonstrative scheme of the transportation of solutes by diffusion resulting from the difference of concentration between points in the soil solution (adapted from COLLAGHAN, 2012).

Finally, COSTA et al. (2009) verified an influence of the soil texture, where soils with greater content of clay present smaller coefficient of P diffusion. This lesser diffusive flow can be explained, in part, by its greater capacity of P adsorption, in great part attributed to presence and reaction with oxides of Fe and Al, in clayey soils (RHEINHEIMER et al., 2003; BASTOS, 2006).

General characteristics of the fertilizers

The evaluation of P available in the soil is generally performed by measuring the degree of energy with which the phosphate is adsorbed to colloidal structures, consequently measuring the soil capacity in replacing the P in the solution, after its absorption by the plants (SANTOS et al., 2008). When the contents in the soil are not sufficient to buffer the solution to critical levels, capable of meeting the plants needs, it is necessary to perform a replacement of nutrients in the solution. The fertilization practice is responsible for elevating the P contents in the soil solution, in such way that supply the deficiency in it.

The physical, chemical and physical-chemical characteristics of fertilizers can interfere in the kinetics of availability of P to plants. In the recommendation of fertilization proposed by the Commission of Chemicals & Soil Fertility of the states of Rio Grande do Sul and Santa Catarina (Comissão de Química e Fertilidade do Solo dos Estados de Rio Grande do Sul e Santa Catarina CQFS-RS/SC, 2004), the doses are established with basis on the quantity of P_2O_5 necessary to achieve an optimum level for plants, established after a series of experiments with several cultures and in different soils. However, this recommendation ignores the relation between the stage of higher nutritional needs of the plant, as the initial (GRANT et al., 2005), and the capacity of the fertilizer in provision it.

Fertilizers that present these characteristics tend to have greater efficiency in the mineral nutrition for plants, where the supplementation of P during the first two to six weeks of growth represent a great impact in the final yield of most crops (GRANT et al., 2001).

The use of commercial fertilizers has grown exponentially worldwide during the late XX century, and following in full expansion in the XXI. As result, several products have appeared in the market, offering a numerous quantity of fertilizers sources, of different physical and chemical forms,

aiming to supply the needs of each environment. Therefore, depending on the mineral content and the industrialization process, the solid fertilizers can differ in size and shape of the particle, as well as color, density, concentration and solubility (MCAULEY, 2009).

The Brazilian legislation demands guarantees as for the chemical composition and physical properties of phosphate fertilizers commercialized in the country, mainly as for the granulometry (size of particles) and weight (CQFS-RS/SC, 2004). Worldwide, most laws are focused in three main specifications: Total P_2O_5 in the fertilizer, physical-chemical properties (solubility) and physical properties (size of particle) (ZAPATA and ROY, 2004).

Thus, physical, chemical and physical-chemical specific characteristics of each fertilizer, under adverse soil conditions, can influence in its efficiency in the plants nutrition. Among these, the solubility (as a physical-chemical characteristic of the fertilizer) presents fundamental importance, deserving greater attention in studies involving the phosphate component (CHIEN et al., 2011).

Solubility in phosphate fertilizers

The solubility of a fertilizer is the measure unit that allows to quantify how much of a certain fertilizer material will dissolve in water and is the most important physical-chemical characteristic, strongly influencing the nutrients availability to plants and the type of fertilizer management to be used (MCAULEY, 2009). Soluble fertilizers will easily dissolve in water, and consequently will be readily available in the soil solution for absorption by the plants. In general, the solubility of a phosphate fertilizer in Brazil is estimated through determinations of total content of P_2O_5 in the fertilizer, P_2O_5 soluble in neutral citrate of ammonium (CNA) + H_2O , P_2O_5 soluble in citric acid at 2% and P_2O_5 soluble in water (RAIJ et al., 2001). The minimum total solubility demanded by the national legislation is 90% for the phosphate sources of high solubility (CHIEN et al., 2009).

Overall, the phosphate sources commercially available are the simple superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and the diammonium phosphate (DAP), which do not have 100% of solubility in water (Table 1). Normally, around 85%-90% of the total P in these fertilizers is soluble in water (CHIEN et

Table 1. Chemical characteristics of the main phosphate fertilizers commercialized in Brazil.

Phosphate Source	P ₂ O ₅ Total	P ₂ O ₅ Citric Acid	P ₂ O ₅ CNA + H ₂ O	P ₂ O ₅ H ₂ O %	Ca	Mg	S
SSP1			18	15	16		8
TSP2			41	36	10		
MAP3			48	44			
DAP4			45	38			
Thermophosphate Mg	17	11			16	7	
Natural Reactive Phosphate	27	30			28		

1Simple Superphosphate; 2Triple Superphosphate; 3Monoammonium phosphate; 4Diammonium Phosphate. Source: adapted from ALCARDE, 1998.

al., 2011). The most common insoluble compounds present in phosphate fertilizers conferring the loss of solubility are generic components of P, such as H8 [(Fe, Al)₃NaH₈(PO₄)₆.6H₂O] in the SSP and H14[(Fe, Al)₃NaH₁₄(PO₄)₈.4H₂O] in the TSP (PROCHNOW et al., 2003a, b).

In a study performed with three different Brazilian SSPs, was found great variability in the presence of insoluble compounds. The solubility in water, and consequent availability of P, of these products was of 46%, 80% and 86%, where is attributed to the presence of the component (Fe, Al)₃NaH₈(PO₄)₆.6H₂O the loss of solubility in the studied fertilizers (PROCHNOW et al., 2003a). CHIEN et al. (2011) point out the need of verification of the fertilizer content in experiments with P, since the TSP is used as standard in experiments of the type (NUNES, 2010) in comparison with other sources, having the possibility of resulting in misconceptions and underestimate the relative efficiency of the sources containing P in the form of calcium phosphate (Ca-P).

In some ways, all the soluble fertilizer sources cited before are rapidly solubilized in soil, providing P in the soil solution for absorption by the plants. Nevertheless, the P soluble in water in the form of orthophosphate can be quickly converted in non soluble forms through reactions with minerals (RHEINHEIMER et al., 2003; BASTOS, 2006). In acid soils, the oxides of Fe and Al can bind specifically with the P of the soil solution, resulting in the formation of insoluble complexes (Fe-P and Al-P). In soils rich in carbonate of Ca and consequently high pH, the P in the soil solution can be adsorbed to the CaCO₃ (Ca-P). Anyhow, the P in the soil solution can precipitate with cations in an amorphous way Fe-P and/or Al-P

in acid soils and such as the Ca-P in alkaline soils of calcareados (CHIEN et al., 2011). All these reactions can result in decrease of the availability of P in the course of time (HEDLEY and MCLAUGHLIN, 2005).

All fertilizers with high quality to solubilize in water should present the same efficiency in making the P available for plants. However, only a limited quantity of studies has been reported on the literature approaching the solubility and agronomic efficiency of different phosphate sources of high solubility, such as the SSP, TSP, MAP and DAP (CHIEN et al., 2011). Therefore, due to the variability of products of the reactions of P in the soil (HEDLEY and MCLAUGHLIN, 2005), different soluble phosphate sources could present different efficiencies depending of the soil chemical characteristics, as an example, the concentration of exchangeable cations.

In a study assessing the efficiency of two phosphate sources, LU et al. (1987) verified that the SSP was more efficient when comparing to the DAP, in the growth of maize crops in soils rich in calcium carbonate, in terms of production of dry mass, absorption by the plant, under different fertilizer managements (superficial, on the sowing row and in greater depth). The authors verified that because of the compound CaHPO₄.2H₂O (main component of the SSP) being more soluble than other Ca-P compounds (formed through the reaction of DAP in a soil rich in calcium carbonate), the SSP presented better efficiency in these chemical conditions of the soil.

However, some researchers have suggested that the nitrification of NH₄-N, present in sources such as the MAP, for NO₃-N (resulting in decrease of pH around the fertilizer granule in the soil) and the absorption of NH₄-N (which increases the acidity

of the rhizosphere) could increase the dissolution of Ca-P precipitated compounds (CHIEN et al., 2011), in this sense increasing the P availability for plants and consequently increase of the fertilizer efficiency. In this case, in soils under no tillage, managed with application system of free sowing, with fertilizers containing the ammoniac component would act in the dissolution and diffusion of Ca-P compounds present in greater concentration in the soil surface. Thus, the reactions and interactions triggered between source-fertilizer and soil are dependent of the soil genetic characteristics, such as mineralogy and texture, and of the used soil management.

Influence of the phosphorus source in P absorption by plants

In its natural form, P is always associated with oxygen ions in the form of phosphate anion (PO_4^{3-}). Therefore, the phosphate ion presents three negative charges capable of reacting with cations in the soil, such as H^+ , Mg^{2+} , Ca^{2+} , Fe^{3+} and Al^{3+} . When the charges are supplied by H^+ ions, there is the chemical balance dynamics in the form of phosphoric acid (H_3PO_4) and also in orthophosphate anions (H_2PO_4^- and HPO_4^{2-}) (RAIJ, 2004). Thus, the relative distribution of these three forms is dependent of the soil pH (Figure 2) (HINSINGER, 2001). The plants roots absorb P ions in

the anionic forms of H_2PO_4^- or HPO_4^{2-} , present in a pH range from 4.0 to 10.0 (BARBER, 1984; HINSINGER, 2001; BARBER, 2002), in which the chemical form of phosphate resultant from the dissolution reaction of fertilizers will exert influence in the P absorption by plants.

The phosphate fertilizers commonly commercialized in Brazil are the MAP, DAP, SST and the TSP, being that the product of its reactions in the soil can generate an environment around the granule of high acidity to alkaline. The pH surrounding the resultant granule of the solubilization of MAP, DAP and TSP is of 3.5, 8.0 and 1.0, respectively (MCAULEY et al., 2009), factor that influences the product of reactions in the soil.

The great capacity of reaction of the phosphate ions with cations present in the soil induces the formation of compounds, in most times, of low solubility and availability for plants. In these conditions, under an acid environment, the formation of complexes with Al^{3+} and Fe^{2+} ions make the P unavailable in the solution and/or favor the formation of H_3PO_4 (non absorbable form). In the same way, under alkaline conditions and high concentrations of Ca^{2+} and Mg^{2+} ions, occurs the precipitation of the phosphate ion in the form of phosphates of Ca and Mg (insoluble compounds) (HOPKINS and ELLSWORTH, 2005).

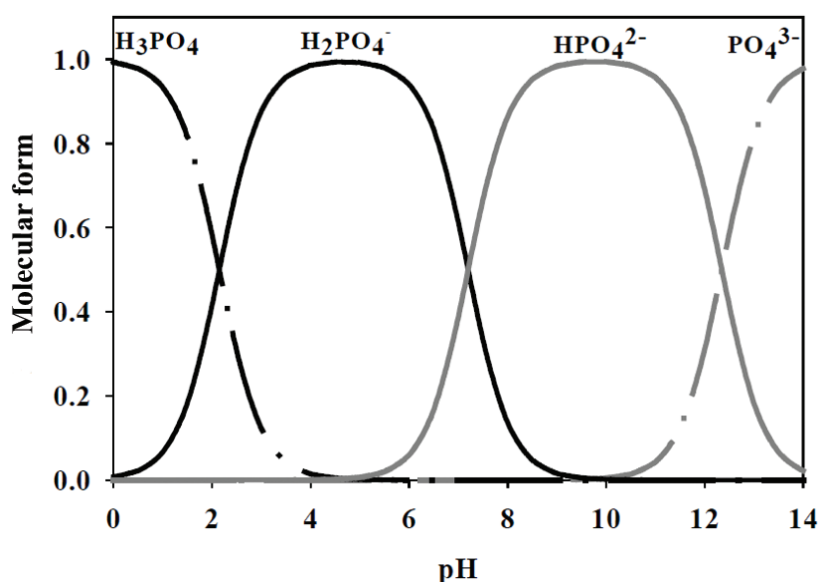


Figure 2. Molecular form of the phosphate ion in chemical balance under different conditions of soil pH (adapted from BARBER, 2002).

Therefore, the reactions resultant from fertilization and the consequent availability of P to plants will be influenced by the phosphate fertilizer sources, which present changes in the pH of the environment around the granule, thus modifying its availability in the soil. Phosphate fertilizers capable of generating environmental conditions of pH (product of dissolution) favorable to formation of anionic forms, preferable absorbable by plants, tend to present greater efficiency in fertilization.

RILEY and BARBER (1971), studying two different nitrogen sources in soybean suggest that the source containing the NH_4^+ molecular structure caused an acidifying effect in the regions of the rhizosphere. The acid environment generated can have contributed for the formation of phosphate ions of easily absorption by the roots and lesser reactions with cations in the soil. In another study, LU et al. (1987) verified better efficiency of the SSP fertilizer when compared to the DAP in soils rich in calcium carbonate. The authors concluded that the compounds generated (through the reaction of DAP in a soil rich in calcium carbonate) presented low solubility, in this sense the SSP presented greater efficiency in these chemical conditions. The alkaline environment generated by the dissolution of the

DAP fertilizer can have contributed for the reactions of the complexation with Ca^{2+} ions, thus forming an insoluble compound.

Therefore, the adequacy of phosphate sources in conditions of soil environment can be a factor that influences the fertilization efficiency, showing that the composition (or physical structure) of each source will have reactions in the soil, allowing greater of lesser relative efficiency of use of the phosphate fertilizer (VASCONCELLOS et al., 1986).

Conclusions

Phosphate fertilizers present characteristics in its molecular composition that must be considered during the moment of agronomic recommendation of fertilization. The possible interference of chemical and physical specific characteristics of the soil and environmental in the product of reactions between fertilizer-soil, can be the main determinant factor of efficiency in the phosphate fertilization.

The better understanding and comprehension of these still little studied matters on the literature, about the influence of the phosphate source in the product of reactions of P in the soil can lead to a more efficient and sustainable fertilizer management.

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